

AD-784 650

MOLECULAR BEAM EPITAXY OF II-VI COM-
POUND WAVEGUIDES

Donald L. Smith

Perkin-Elmer Corporation

Prepared for:

Office of Naval Research
Advanced Research Projects Agency

22 July 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

TECHNICAL REPORT

1 March 1974 - 30 June 1974

ARPA Order No. 2327

Contract No. N00014-73-0280^c

Program Code No. 3D10

Principal Investigator:
Dr. Donald L. Smith
203-762-6916

Contractor:
Perkin-Elmer Corporation

Scientific Officer:
Director, Naval Research
Laboratory

Effective Date of Contract: Title: Molecular Beam Epitaxy
1 March 1973 of II-VI Compound
(received 28 June 1973) Waveguides

Contract Expiration Date:
30 June 1974

Amount of Contract: \$67,000.00

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U.S. Government

Sponsored by

Advanced Research Projects Agency

ARPA Order No. 2327

TABLE OF CONTENTS

I. Introduction	1
II. Results	
A. SEM Examination	1
B. Substrate Preparation	2
C. ZnSe Growth	3
D. ZnTe Growth	5
III. Conclusions	5
Figures	8
References	10

Unclassified

AD 784 650

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) MOLECULAR BEAM EPITAXY OF II-VI COMPOUND WAVEGUIDES		5. TYPE OF REPORT & PERIOD COVERED Technical Report 1 March - 30 June, 1974	
7. AUTHOR(s) Dr. Donald L. Smith		6. PERFORMING ORG. REPORT NUMBER 12012	
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Perkin-Elmer Corporation Optical Group Research Department Norwalk, Conn. 06856		8. CONTRACT OR GRANT NUMBER(s) N00014-73-C-0280	
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Advanced Research Projects Agency Office of Naval Research		12. REPORT DATE July 22, 1974	
		13. NUMBER OF PAGES 10 14	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) epitaxy; vacuum evaporation, II-VI semiconductors; optical waveguides Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U.S. Department of Commerce Springfield VA 22151			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Monocrystalline films of ZnSe and ZnTe have been grown by molecular beam epitaxy on GaAs(110) and (100) at 300 to 350°C. ZnTe(100) films are as smooth as the chemically-polished substrate (smooth to tens of Angstroms), while the others are considerably rougher. Films grown on BaF ₂ (100) are poly- crystalline. ZnTe/Zn(SeTe)/GaAs(100) is proposed for an optical waveguide system.			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

I. INTRODUCTION

II-VI compounds have considerable potential as electro-optic modulators in integrated optical circuits. The goal of our program has been to grow by molecular beam epitaxy (MBE) monocrystalline II-VI films of sufficient smoothness, purity, and crystallographic perfection to behave as low-loss waveguides.

The last report, submitted March 25, 1974, summarized work done since the start of the program, including substrate preparation, calibration and control of source material evaporation, film growth on $\text{CaF}_2(111)$, $\text{CdS}(0001A)$ and $\text{CdSe}(0001A)$, and waveguiding measurements. The general findings were that at lower growth temperatures films were smooth but polycrystalline and at higher temperatures they were monocrystalline but rough. Waveguiding was demonstrated in ZnSe and ZnTe , but propagation losses were unacceptably high.

The present report discusses work performed since March 1, 1974, in which the effects of substrate orientation and structure on film growth morphology have been examined in an attempt to achieve smoother monocrystalline films. Growth of ZnSe and ZnTe on $\text{GaAs}(110)$ and (100) were studied in particular detail.

II. RESULTS

A. SEM EXAMINATION

A sampling of films grown on $(0001A)$ substrates was

examined by a scanning electron microscope with the hope that the structural details of the film surfaces might give a clue as to the preferred growth plane, but the available 400⁰Å resolution was insufficient for this purpose.

B. SUBSTRATE PREPARATION

Substrates employed included BaF₂(100), CdS(0001B), and GaAs(110) and (100). A chemical polishing procedure for BaF₂(100) which generates surfaces completely featureless under 400X Nomarski microscope examination had been developed in another program. Equally smooth surfaces were found under the present contract to be obtainable on CdS(0001B) using 4 parts of 2 1/2% sodium hypochlorite (liquid household bleach diluted 1:1 with water) to 1 part precipitated silica. Procedures were similar to those reported for CdS(0001A).¹ GaAs was polished with Mirrolite (Materials Development Corp.), but better results were obtained by using 90% of the recommended concentration. While resulting surfaces were mirror-smooth to the eye, they had a slight texture under Nomarski examination (perhaps tens of Angstroms).

BaF₂(100) substrates produced good LEED (low-energy electron diffraction) patterns after 600°C, 1 minute heat-cleaning at 10⁻⁹ Torr. CdS(0001B) substrates gave patterns indicating considerable disorder and faceting after either heat-cleaning or ion-bombardment under various conditions. Since no appreciable contamination was detectable by Auger

spectroscopy, it was concluded that CdS(0001B) must be a thermodynamically unstable surface and therefore unsuitable for epitaxy. GaAs heat-cleaned at 600°C gave LEED patterns which were well-ordered but which also had high diffuse background due to the residual surface carbon which is typical of lower-bandgap semiconductors and of metal surfaces. The background was somewhat reduced by ion bombardment, but this procedure did not noticeably improve epitaxy, and the carbon was always readily buried by the growing film. Therefore, GaAs was generally only heat-cleaned.

C. ZnSe GROWTH

We had heretofore grown II-VI compounds by evaporating the elements rather than the compounds because these were obtainable in higher purity and because we wished to examine the effect of II/VI evaporation rate ratio on film growth. Selenium, however, is a difficult element to handle under vacuum, having a vapor pressure of 10^{-4} Torr at only 165°C, and in addition existing as a multitude of polyatomic molecules³ which influence sticking coefficient and flux monitoring. ZnSe was therefore grown here from 5-nines Eagle-Picher ZnSe crystallites. Deposition rate was calculated from the reported $(\text{ZnSe})_s \rightleftharpoons \text{Zn}_g + 1/2(\text{Se}_2)_g$ equilibrium constant,⁴ using the Knudsen effusion equation and system geometry as discussed previously,⁵ and is plotted in Figure 1. Actual growth rate was about 1/5 of that calculated; this fraction is plotted as "sticking coefficient" in Figure 2a. Moreover, the Se/Zn flux ratio measured by the mass spectrometer here was about 1/5 of

that measured previously in growth from the elements when Se/Zn had been "balanced" by the quartz crystal technique⁵. These observations suggest that the sticking coefficient of Se is about 1/5 at the ZnSe growth temperature, and that the "balanced" Se/Zn ratio in growth from the elements actually amounted to a X5 excess of impinging Se.

General trends in crystallographic and topographic quality of ZnSe films grown on GaAs(110) and (100) are plotted as functions of growth temperature in Figure 2a, "1" representing very sharp LEED patterns with zero diffuse background and completely featureless surfaces under 400X Nomarski examination, "0" representing no LEED patterns and surfaces rough to the eye. From 300 to 350°C, films grew epitaxially and LEED patterns were very good on both (110) and (100). These patterns were always better than those from the substrate, and in two cases where no pattern was observable from the (100) substrate, good (100) LEED patterns were still obtained from the films. Under the same conditions, ZnSe grew polycrystalline on a BaF₂(100) substrate.

All ZnSe films on GaAs(110) and all films thicker than 1/4 micron on GaAs(100) were rougher than the substrate, becoming worse with increasing substrate temperature as indicated on Figure 2a. Roughness increased with thickness, and films thicker than 1 micron were rough to the eye. For similar conditions, films were rougher on (110) than (100).

The results of Figure 2a were the same at both 1/3 and 3 microns/hour growth rate.

D. ZnTe GROWTH

ZnTe was grown from the elements, as previously,⁵ at 2 microns/hour. Figure 2b shows sticking coefficient, crystallography and topography as Figure 2a did for ZnSe. Sticking coefficient was unity up to 350°C, and high quality epitaxy was obtained from 300 to 350°C on both GaAs(110) and (100). It should be noted that under the same conditions, ZnTe had grown polycrystalline on both BaF₂(100) and CaF₂(100) in October, 1973 (not reported previously). These results are consistent with those for ZnSe on BaF₂(100), above. 1 micron-thick films on GaAs(100) were as smooth as the substrate, and on (110) were somewhat rougher, though still smooth to the eye.

A series of two-layer films, ZnTe on ZnSe, were grown on GaAs(110) and (100) as potential waveguide systems, the ZnSe acting as a low-index ($n=2.6$) buffer layer between the ZnTe guide ($n=3.0$) and the high-index GaAs ($n=3.6$). ZnTe on a 1/10 micron ZnSe(100) film was as smooth as the substrate, but the buffer layer was too thin to allow propagation of 6328Å light. ZnTe on 1/10 micron of ZnSe(110) and on 3/4 micron of ZnSe(110) and (100) was rough to the eye and could not be coupled into.

III. CONCLUSIONS

Substrate orientation and structure appear to be key

factors in II-VI compound growth. While epitaxy of ZnSe and ZnTe has been obtained in this laboratory on all three basic cubic planes, the required conditions and the film topography vary considerably from plane to plane. On (100), epitaxy has been obtained for GaAs but not for BaF_2 or CaF_2 substrates. By comparison, Holt⁶ obtained epitaxial ZnTe by vacuum evaporation on $\text{CaF}_2(111)$ and $\text{BaF}_2(111)$ but not on NaCl (100). Epitaxy of ZnSe by vacuum evaporation on GaAs(100) has been reported by other workers⁷, but only above 350°C, possibly because of their less hard vacuum conditions (10^{-6} vs. 10^{-9} Torr). Film smoothness is a strong function of substrate plane; in order of decreasing smoothness, $(100) > (110) \gg (111)$. The temperature range for epitaxy is also much narrower on (111) than on the other planes. A similar trend has been found for ZnSe vacuum evaporation on Ge⁸, where the temperature range of epitaxy decreased as follows: $(100) > (110) > (111)$, (111) giving no epitaxy.

In summary, (100) is clearly the preferred plane for ZnSe and ZnTe epitaxy by vacuum evaporation, but for zincblende and not for fluorite or rocksalt-structure substrates. Since zincblende crystals are noncentrosymmetric and since the consequent internal field components are stronger parallel to (100) planes than to (110) or (111), perhaps it is the presence of these parallel field components which is the critical factor in encouraging epitaxy. Strangely, the situation for liquid phase epitaxy of ZnTe on ZnSe is the opposite: (111) films are much smoother than (110) or (100) films.⁹

For further MBE work directed at waveguide modulators, a system based on ZnTe rather than on ZnSe is preferable for several reasons: far smoother monocrystalline ZnTe films

can be grown, Se is difficult to handle in MBE, and ZnTe has twice the electrooptic coefficient of ZnSe. The substrate should be InAs(100), whose lattice constant matches ZnTe much more closely than does that of GaAs. The second layer of the required two-layer film would be $\text{ZnSe}_x\text{Te}_{1-x}$ or $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$, where $x \rightarrow 0$.

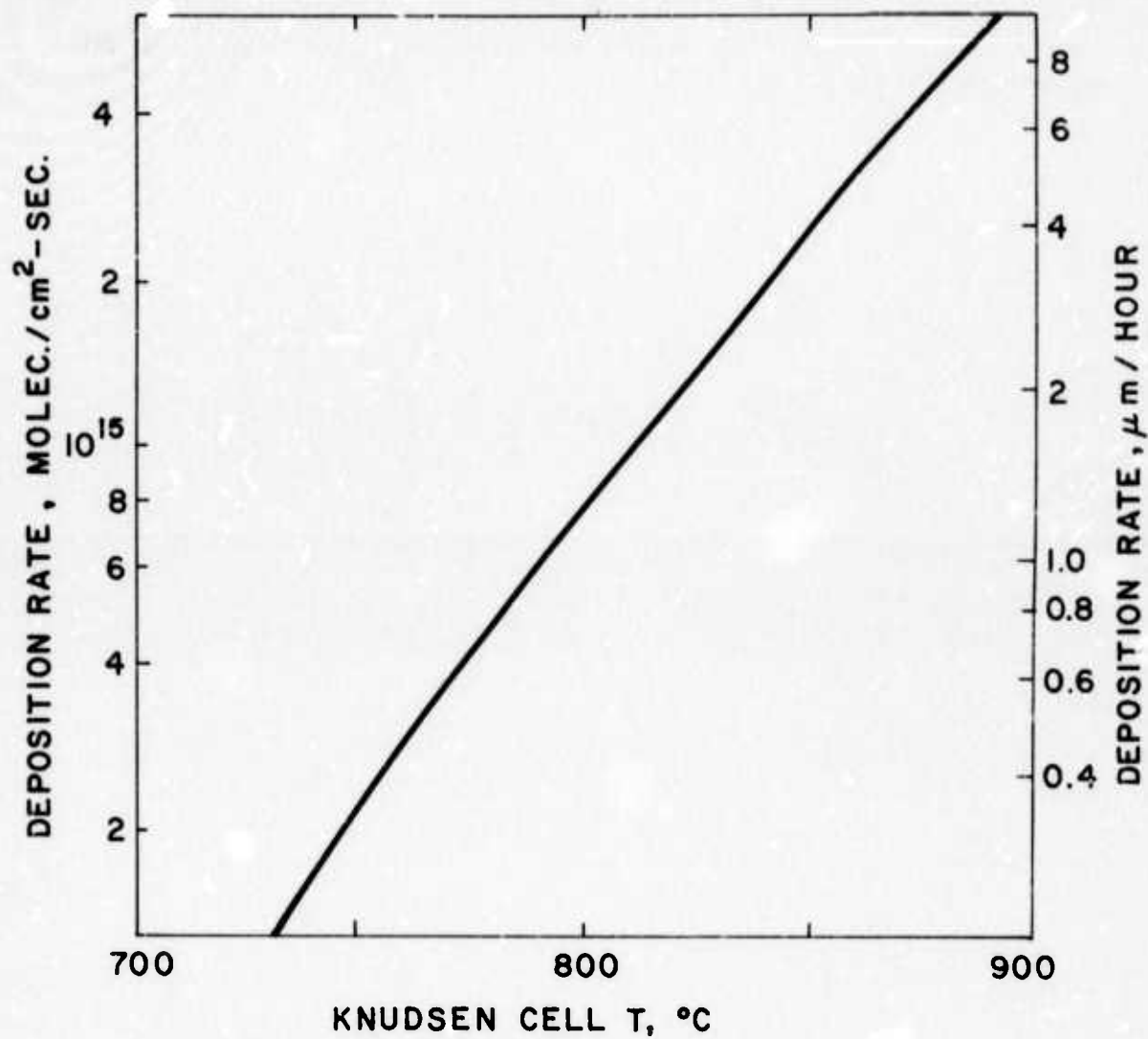


FIG. 1 ZnSe EVAPORATION
(3mm dia. orifice, 5cm substrate distance)

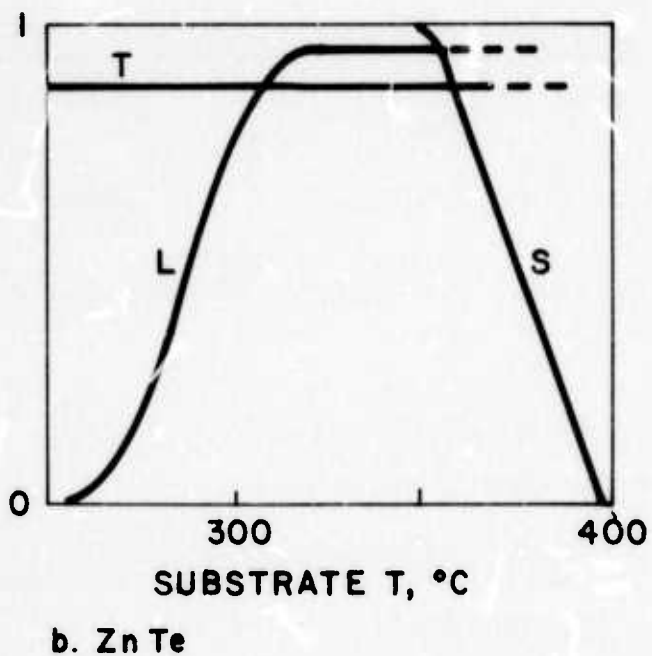
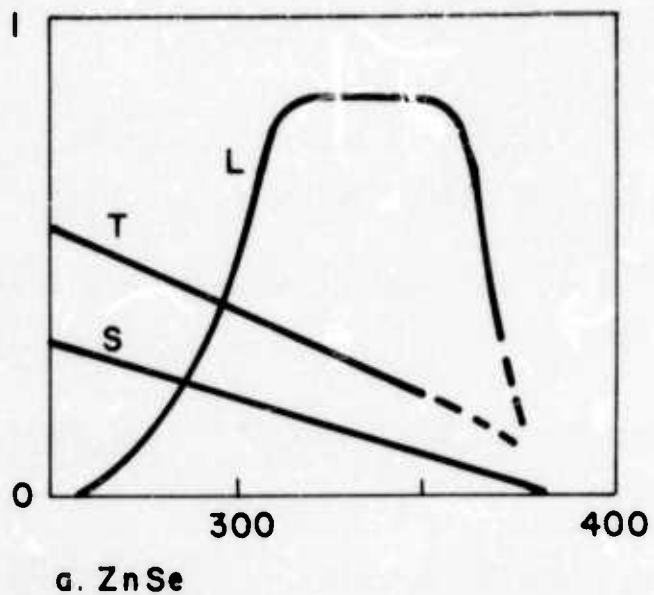


FIG. 2 GROWTH CHARACTERISTICS ON GaAs
(L=LEED Pattern quality, T= Topographic
quality, S= Sticking coefficient)

REFERENCES

1. Vincent Y. Pickhardt and Donald L. Smith; J. Electrochemical Soc; August, 1974.
2. Richard E. Honig and Dean A. Kramer; RCA Review, 30, 285(1969).
3. J. Berkowitz and W. A. Chupka; J. Chem. Phys. 48, 5743(1968).
4. P. Goldfinger and M. Jeunehomme; Trans. Faraday Soc. 59, 2851(1963).
5. Donald L. Smith; "Molecular Beam Epitaxy of II-VI Compound Waveguides", ARPA contract no. N00014-73-0280, report of March 25, 1974.
6. D. B. Holt; Brit. J. Appl. Phys. 17, 1935(1966).
7. J. E. Genthe and R. E. Aldrich; Thin Solid Films 8, 149(1971).
8. J. T. Calow, D. K. Kirk, and S. J. T. Owen; Thin Solid Films, 9, 409(1972).
9. S. Fujita, F. Moriai, S. Arai, and T. Sakaguchi; J. Appl. Phys. 12, 1841(1973).